ABC of DFT: Hands-on session 1
Introduction into calculations on molecules

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Wann? 09.11.2012, 11:30-13:00
Wo? KIT Campus Nord, Flachbau Physik, Geb. 30.22, Computerpool, Raum FE-6
Preliminary remarks (schedule)

- First 5 hands-on sessions (09.11, 16.11, 23.11, 30.11, 07.12): **TURBOMOLE package**
  - molecules: structure optimization, visualization of orbitals and charge densities, ionization energies & electron affinities, molecular vibrations, simulation of IR spectra, etc.

- Next 5 hands-on sessions (14.12, 18.01, 25.01, 01.02, 08.02): **FHI-aims package**
  - Periodic (3D & 2D) systems: density of states and band structure of metals & semiconductors, structure optimization, visualization of charge densities, ferromagnetic systems, graphene, work functions, defects and phonons, etc.
Overview

- Electronic structure methods for molecules
  - Reminder: Kohn-Sham formulation of DFT
  - Basis set approximation: Gaussian type orbitals

- TURBOMOLE
  - Functionality & usage philosophy

- Creating input, performing self-consistent calculation, geometry optimization
  - “Warm-up” examples: H atom, H₂ molecule
  - Do it yourself: N₂, O₂ molecules
Reminder: Kohn-Sham formulation of DFT

- Ansatz for the electron density:

\[ n(r) \overset{\text{def.}}{=} n_s(r) = \sum_{i=1}^{N_{\text{el.}}} |\varphi_i(r)|^2 \]

- Schrödinger like, Kohn-Sham equations:

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_s(r) \right] \varphi_i(r) = \varepsilon_i \varphi_i(r)
\]

\[ V_s(r) = V_{\text{ext/ions}}(r) + \int \frac{e^2 n_s(r)}{|r - r'|} d^3 r' + V_{\text{XC}}[n_s(r)] \]

external potential  Hartree potential  “exchange & correlation” potential
Solving KS equations: basis set approximation

- Each Kohn-Sham molecular orbital $\varphi_i$ (MO) is expanded in terms of atom-centered basis functions $\chi_\alpha$ (“atomic orbitals”):

$$\varphi_i(r) = \sum_{\alpha} \chi_\alpha(r) C_{\alpha i}$$

- KS equations take form of the eigenvalue problem (many powerful algorithms exist to solve it):

$$HC = SC \varepsilon$$

$$H_{\alpha\beta} = \left\langle \chi_\alpha \left| -\frac{\hbar^2}{2m} \nabla^2 + V_s(r) \right| \chi_\beta \right\rangle \rightarrow \text{Hamiltonian}$$

$$S_{\alpha\beta} = \left\langle \chi_\alpha \left| \chi_\beta \right\rangle \rightarrow \text{Overlap integrals}$$
Gaussian basis sets: typical choice in quant.chem.

- **Gaussian type orbitals (GTO)**

  \[ f^{\text{GTO}}(r) = \left( \frac{2\alpha}{\pi} \right)^{3/4} \exp\left( -\alpha r^2 \right) \]

- **Contracted GTOs (CGTOs)**

  \[ \chi_{\alpha}(r) = \left[ c_1 f^{\text{GTO}}(\alpha_1, r) + c_2 f^{\text{GTO}}(\alpha_2, r) + \ldots \right] Y_{lm}(\hat{r}) \]

- **Split valence (SV) basis sets**: electrons are partitioned in core and valence types.
  - Each **core** electron: one contracted Gaussian orbital
  - For every **valence** electron: two, three, etc ... contracted GTOs: so-called, double-$\zeta$ (SV), triple-$\zeta$ (TZV), ... basis sets

- **Polarization effects** are accounted for by adding **polarization (P) basis functions**, which have larger angular momentum $l$ numbers: SVP, TZVP, etc... basis sets
Closed shell and open shells systems

**Even** number of electrons: “closed shell”

- Virtual orbitals
- Occupied orbitals

**Odd** number of electrons: “open shell”

- Virtual orbitals
- Occupied orbitals

**Constrain**: up-spin and down-spin orbitals are identical: \( V_{xc}[n(r)] \)

**No constrain**: up-spin and down-spin orbitals are optimized independently: \( V_{xc}[n^\uparrow(r), n^\downarrow(r)] \)
TURBOMOLE: functionality

- One of the fastest quantum chemistry packages
  developed by Prof. Ahlrichs group (Uni Karlsruhe)

- optimized Gaussian-type basis sets, real space formulation
  (molecules, clusters)
- all symmetry point groups

- DFT: various exchange-correlation (xc) functionals
- wave function methods: Hartree-Fock (HF) and post-HF levels of theory
- various ground and excited state properties: bond lengths & angles,
  excitation energies, vibrational spectra: infrared & Raman, NMR
  shieldings, response functions, etc …
- simulation of environment: solvation effects, ionic crystals
- parallel runs: simulations with hundreds of atoms
TURBOMOLE: usage philosophy

- The usage of TURBOMOLE is UNIX/Linux oriented:
  - command line driven
  - many different programs (modules), each one specialized for particular methods and/or properties
  - scripts are used to combine the functionalities and manage workflows
  - Input file(s) can be changed by Linux editors
  - output is processed by standard Linux tools (editors, grep, awk ...)

- Hence: some (basic) Linux skills are required!
Getting into practice ...

- A user account is available for you on the Linux cluster (placed at INT) called intact: please, see a separate sheet given to you.

- Required software (TURBOMOLE binaries and scripts, visualization tools, etc.) is accessible for you: $PATH variable is set in .bashrc file.

- You can find a documentation (including this tutorial & TURBOMOLE manual, and also FHI-aims manual) at ~/ABC_of_DFT/hands-on-sessions/documentation.

- You can find set of basic exercises at ~/ABC_of_DFT/hands-on-sessions/session.1.

- Each basic exercise contains full output data (e.g., ~/example.2.h2/output.h2), so that you'll be able to compare your results with expected ones.
**Example 1 – H atom**

- We start with the simplest possible system: H atom
- Go to directory
  ```bash
cd ~/ABC_of_DFT/hands-on-sessions/session.1/example.1.h
  
  sessions/session.1/example.1.h
  ```
- Create your own directory where you are going to run a calculation:
  ```bash
cp -r structure.h my.h.atom
  
  cd my.h.atom
  ```
- A file `coord` is reserved for atomic positions. In our case, there is a single H atom. Type:
  ```bash
cat coord
  ```
  ```
  $coord
  0.000000000000000  0.000000000000000  0.000000000000000 h
  $end
  ```
- Remark: atomic positions are given in atomic units (1 a.u. = 0.529 Å)
Example 1 – H atom: creating an input (step 1)

- Interactive module **define** is used to set-up system specific parameters for the calculation. Type from the command line: **define**
  
  ...  
  DATA WILL BE WRITTEN TO THE NEW FILE control  
  IF YOU WANT TO READ DEFAULT-DATA FROM ANOTHER control-TYPE FILE,  
  THEN ENTER ITS LOCATION/NAME OR OTHERWISE HIT >return<.  

- Hit `<Enter>` for the name of input file

- **INPUT TITLE OR**
  
  ENTER & TO REPEAT DEFINITION OF DEFAULT INPUT FILE

Type e.g. **h atom** for the title, followed by `<Enter>`

- You will get the „molecular geometry“ menu

  SPECIFICATION OF MOLECULAR GEOMETRY ( #ATOMS=0 SYMMETRY=c1 )
  YOU MAY USE ONE OF THE FOLLOWING COMMAND
  sy <group> <eps> : DEFINE MOLECULAR SYMMETRY (default for eps=3d-1)
  desy <eps> : DETERMINE MOLECULAR SYMMETRY AND ADJUST
  COORDINATES (default for eps=1d-6)
  susy : ADJUST COORDINATES FOR SUBGROUPS
  ai : ADD ATOMIC COORDINATES INTERACTIVELY
  a <file> : ADD ATOMIC COORDINATES FROM FILE <file>

  ....

Type **a coord** `<Enter>` to append a single H atom
Example 1 – H atom: creating an input (step 2)

You will see that 1 atom has been added:

```
CARTESIAN COORDINATES FOR 1 ATOMS HAVE SUCCESSFULLY BEEN ADDED.

... ...
SPECIFICATION OF MOLECULAR GEOMETRY ( #ATOMS=1 SYMMETRY=c1 )
YOU MAY USE ONE OF THE FOLLOWING COMMAND
sy <group> <eps> : DEFINE MOLECULAR SYMMETRY (default for eps=3d-1)
desy <eps> : DETERMINE MOLECULAR SYMMETRY AND ADJUST COORDINATES (default for eps=1d-6)
susy : ADJUST COORDINATES FOR SUBGROUPS
ai : ADD ATOMIC COORDINATES INTERACTIVELY
a <file> : ADD ATOMIC COORDINATES FROM FILE <file>
... *
: TERMINATE MOLECULAR GEOMETRY SPECIFICATION
   AND WRITE GEOMETRY DATA TO CONTROL FILE
```

IF YOU APPEND A QUESTION MARK TO ANY COMMAND AN EXPLANATION OF THAT COMMAND MAY BE GIVEN

Nothing to be done any more in the “molecular geometry” menu. To proceed, type

```
* <Enter>
```
Example 1 – H atom: creating an input (step 3)

- We come to „atomic attributes“ menu:

  ATOMIC ATTRIBUTE DEFINITION MENU ( #atoms=1   #bas=1   #ecp=0   )

  b    : ASSIGN ATOMIC BASIS SETS
  bb   : b RESTRICTED TO BASIS SET LIBRARY
  bl   : LIST ATOMIC BASIS SETS ASSIGNED

  ...

  *    : TERMINATE THIS SECTION AND WRITE DATA OR DATA REFERENCES TO control
  GOBACK=& (TO GEOMETRY MENU !)

- You may check that a default basis set def-SV(P) is assigned:

  bl <Enter>

  INDEX | BASIS SET NICKNAME
  ----- | --------------------------
  1     | h def-SV(P)

  To proceed for the next menu, type
  * <Enter>
Example 1 – H atom: creating an input (step 4)

- Within next menu define provides initial molecular orbitals (in our case, atomic orbitals) with, e.g., an extended Hückel guess.

**OCCUPATION NUMBER & MOLECULAR ORBITAL DEFINITION MENU**

**CHOOSE COMMAND**

- infsao : OUTPUT SAO INFORMATION
- eht : PROVIDE MOS & OCCUPATION NUMBERS FROM EXTENDED HUECKEL GUESS
- use <file> : SUPPLY MO INFORMATION USING DATA FROM <file>
- man : MANUAL SPECIFICATION OF OCCUPATION NUMBERS
- hcore : HAMILTON CORE GUESS FOR MOS
- & : MOVE BACK TO THE ATOMIC ATTRIBUTES MENU

THE COMMANDS use OR eht OR * OR q(uit) TERMINATE THIS MENU !!!
FOR EXPLANATIONS APPEND A QUESTION MARK (?) TO ANY COMMAND

To choose the Hückel guess, type

**eht <Enter>**

- You will be asked further questions: accept all defaults (among them are default zero charge & occupation of one orbital with one spin)
Example 1 – H atom: creating an input (step 5)

- You will come to the last, “general menu”:

  GENERAL MENU: SELECT YOUR TOPIC
  scf: SELECT NON-DEFAULT SCF PARAMETER
  mp2/cc2: OPTIONS AND DATA GROUPS FOR MP2, CC2, ETC.
  ex: EXCITED STATE AND RESPONSE OPTIONS
  prop: SELECT TOOLS FOR SCF-ORBITAL ANALYSIS
  drv: SELECT NON-DEFAULT INPUT PARAMETER FOR EVALUATION
       OF ANALYTICAL ENERGY DERIVATIVES
       (GRADIENTS, FORCE CONSTANTS)
  rex: SELECT OPTIONS FOR GEOMETRY UPDATES USING RELAX
  stp: SELECT NON-DEFAULT STRUCTURE OPTIMIZATION PARAMETER
  e: DEFINE EXTERNAL ELECTROSTATIC FIELD
  dft: DFT Parameters

  ...

- Choose DFT, by entering dft <Enter>, and then on <Enter>

  STATUS OF DFT_OPTIONS:
  DFT is used
  functional b-p
  Default “b-p” functional is GGA BP86 by Becke and Perdew

  Just <ENTER>, q or '*' terminate this menu.

  Type q <Enter> to quit and go back to the “general menu”

- Nothing to be done any more for H atom, type q <Enter> to finish your session with define
Example 1 – H atom: creating an input (remarks)

- After **define** session is finished, you’ll find several files in your directory: `control`, `basis`, `alpha`, `beta`.

- File **control** contains all settings to control over your calculation. If required, changes to it can be done using standard UNIX editors (like `vim` or `emacs`).

- File **basis** contains information about basis functions (contracted Gaussian type orbitals) to be used for the expansion of the wave functions.

- Files **alpha & beta** contain energies and expansion coefficients of atomic orbitals over the basis functions, for up- and down-spin electrons (in case of molecules, molecular orbitals & their energies).
Example 1 – H atom: running calculation

- To run a DFT calculation, call a `dscf` module: `dscf`
- Scroll up output data: you’ll find, a calculation is finished within 5 iterations
- Data post-processing script `eiger` provides information about orbital energies and occupations. Type: `eiger > atomic.levels.dat` and afterwards: `cat atomic.levels.dat`

```
h atom
Total energy = -0.4989430987 H = -13.5769402 eV
HOMO-LUMO Separation
  HOMO: 1. a  1 a  -0.27623884 H =  -7.51685 eV
  LUMO: 2. b  1 a  -0.04813878 H =   -1.30992 eV
  Gap : +0.22810006 H =      +6.20692 eV
Number of MOs=  4, Electrons=  1.00, Symmetry: c1

   Nr.  Orbital  Occupation  Energy
   4.  b    2 a         +0.624165 H =      +16.984 eV
   3.  a    2 a         +0.383478 H =      +10.435 eV
   2.  b    1 a    -0.048139 H =      -1.310 eV
   1.  a    1 a   1.000  -0.276239 H =    -7.517 eV
```

- Compare the energy of a single occupied orbital with the ionization potential for H atom (-13.6 eV). Why there is a difference?
Example 2 – \( \text{H}_2 \) molecule: creating input

- Structure of a hydrogen molecule can be found at:
  ```
  cd ~/ABC_of_DFT/hands-on-sessions/session.1/example.2.h2
  ```

- Create a new directory:
  ```
  cp -r structure.h2 h2.molecule
  cd h2.molecule
  ```

- Positions (in atomic units) of two H hydrogen atoms are written to file `coord` (type, `cat coord`):
  ```
  $coord
  0.000000000000000 0.000000000000000 0.000000000000000 h
  0.000000000000000 0.000000000000000 1.400000000000000 h
  $end
  ```
Example 2 – H₂ molecule: creating input

- Run **define** module, create an input for H2, similar to that for H atom
- In the “molecular geometry menu”, append your structure with

  a coord <Enter>

  CARTESIAN COORDINATES FOR 2 ATOMS HAVE SUCCESSFULLY BEEN ADDED.

  SPECIFICATION OF MOLECULAR GEOMETRY ( #ATOMS=2 SYMMETRY=c1 )

REMEMBER, YOU MAY USE ONE OF THE FOLLOWING COMMANDS:

- **sy <group> <eps>** : DEFINE MOLECULAR SYMMETRY (default for eps=3d-1)
- **desy <eps>** : DETERMINE MOLECULAR SYMMETRY AND ADJUST COORDINATES (default for eps=1d-6)
- **susy** : ADJUST COORDINATES FOR SUBGROUPS
- **ai** : ADD ATOMIC COORDINATES INTERACTIVELY
- **a <file>** : ADD ATOMIC COORDINATES FROM FILE <file>
- **aa <file>** : ADD ATOMIC COORDINATES IN ANGSTROEM UNITS FROM FILE <file>
- **sub** : SUBSTITUTE AN ATOM BY A GROUP OF ATOMS
- **i** : INTERNAL COORDINATE MENU
- **ired** : REDUNDANT INTERNAL COORDINATES

- To make possible atomic structure relaxations, switch on “internal coordinates”:

  ired <Enter>
Example 2 – H₂ molecule: creating input

- You’ll see a message like that:

```
GEOSPY:  NBDIM:       1  NDEGR:       1
  Lowest Eigenvalue of BmBt is:          2.0000000000
GEOSPY:  ATTENTION!
  natural internals not linearly independent?
  Decoupling with "globtry"= 0.999999999990000000
  Lowest Eigenvalue of projected BBt      2.0000000000 No:   1
  Quotient of Eigenvalues                  1.0000000000
  OCCUPATION OF BLOCKS:                   1 0 0 0 0 0

SPECIFICATION OF MOLECULAR GEOMETRY ( #ATOMS=2  SYMMETRY=c1 )
YOU MAY USE ONE OF THE FOLLOWING COMMANDS :
sy  <group>  <eps>   : DEFINE MOLECULAR SYMMETRY (default for eps=3d-1)
desy  <eps>    : DETERMINE MOLECULAR SYMMETRY AND ADJUST
               COORDINATES (default for eps=1d-6)
susy              : ADJUST COORDINATES FOR SUBGROUPS
ai                : ADD ATOMIC COORDINATES INTERACTIVELY
...
```

- To proceed, type
  * `<Enter>`

- Continue a define session, following instructions at slides 14-16.
**Example 2 – H$_2$ molecule: running calculation**

- Perform a DFT calculation, analyze your output. Type
  
  ```
dscf <Enter>
eiger > molecular.levels.dat <Enter>
cat molecular.levels.dat <Enter>
  ```

- Your results will look like:

  ```
h2 molecule
Total energy = -1.1693659559 H = -31.8200848 eV

HOMO–LUMO Separation
HOMO: 1. 1 a -0.38338626 H = -10.43248 eV
LUMO: 2. 2 a +0.05883434 H = +1.60096 eV
Gap : +0.44222060 H = +12.03344 eV

Number of MOs= 4, Electrons= 2.00, Symmetry: c1

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Orbital</th>
<th>Occupation</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.</td>
<td>4 a</td>
<td>2.000</td>
<td>+0.737992 H = +20.082 eV</td>
</tr>
<tr>
<td>3.</td>
<td>3 a</td>
<td></td>
<td>+0.313745 H = +8.537 eV</td>
</tr>
<tr>
<td>2.</td>
<td>2 a</td>
<td></td>
<td>+0.058834 H = +1.601 eV</td>
</tr>
<tr>
<td>1.</td>
<td>1 a</td>
<td>2.000</td>
<td>-0.383386 H = -10.432 eV</td>
</tr>
</tbody>
</table>
Example 2 – $\text{H}_2$ molecule: remarks

- A default basis set, def-SV(P), which we have used, ascribes two basis functions (per spin) per H atom: in case of $\text{H}_2$ molecule, we get four spin-degenerate molecular orbitals: one being occupied by two electrons, and three virtual, empty orbitals.

- A measured ionization energy of $\text{H}_2$ molecule is 15.4 eV. For the exact (but unknown!) XC functional, the HOMO (highest occupied molecular orbital) energy would give the value of the ionization potential (up to minus sign): statement known as Koopman’s theorem.

Our value (10.4 eV) significantly underestimates the ionization energy: that is a common problem with all approximate DFT XC-functionals, which are based on the local density approximation (LDA) and its gradient corrections (GGA).
Example 2 – H₂ molecule: potential energy surface

- Computing the energy of H-H dimer as function of a distance between H atoms gives us a potential energy surface and allows to estimate the H-H bond length. Let us check, how DFT performs in this case.

- Make a new directory, say
  ```
  cd ~/ABC_of_DFT/hands-on-sessions/session.1/example.2.h2
  mkdir h2.energy
  ```

- A script `h2` (located at your `~/bin` directory) creates automatically an input and runs the DFT calculation for several H-H distances. Simply type from a command line: `h2`, and read a short description.

- As input, the script takes an abbreviation of the TURBOMOLE basis set. Accepted sets are: def-SVP (2 basis functions per H atom), def-TZVP (6 basis functions), and def-QZVP (30 basis functions).
Example 2 – H$_2$ molecule: potential energy surface

- Perform calculations with different basis sets. Type
  
  ```
  h2 def-SVP  (output will follow up …)
  h2 def-TZVP
  h2 def-QZVP
  ```

- Results of your calculations will be sorted into three different directories and three output .dat-files. Check any of them, type
  
  ```
  cat energy.profile.def-SV(P).dat
  ```

  ```
  #dist[a.u.]   E[eV].def-SV(P)
  .75         -25.5655107
  1.0         -30.0952703
  1.5         -31.8268463
  2.0         -31.0131306
  2.5         -29.8140698
  3.0         -28.7179669
  4.0         -27.1254815
  5.0         -26.2018811
  #end
  ```

  ---> A value being close to the H-H bond length (1.40 a.u.)
Example 2 – H₂ molecule: potential energy surface

- With another script `h2plot`, you can view results of calculations for the three different basis sets.
- Type from a command line: `h2plot`. A window will appear:

![Graph showing potential energy surface for H₂ molecule with different basis sets.]

**Question:** with larger basis set, we get lower values of energy. Why?
Example 2 – H$_2$ molecule: structure optimization

An automatic structure optimization is possible with help of shell script `jobex`, which calls subsequently modules for the electronic energy calculation, gradient and, based on that, estimates the new coordinates.

To perform a geometry optimization of H$_2$, take one of your calculations [say, with $d$(H-H)=2.0 a.u.] and make a new directory:

```bash
    cd results.def-SV\(P\)
    cp -r d_2.0 h2.relaxed
    cd h2.relaxed
```
Example 2 – H₂ molecule: structure optimization

- Structure optimization is controlled by the script `jobex`; type from a command line: `jobex`

- Few steps are required, until the energy gradient approaches zero. Type: `grep cycle gradient`
  Do you understand results?

- Optimized geometry of the molecule is saved to file `coord`. Check it: what is the equilibrium H-H bond length which you’ve got?
Example 2 – H₂ molecule: structure optimization

- Print out the orbital energies. Type:
  ```
eiger > molecular.levels.relaxed.dat
cat molecular.levels.relaxed.dat
  ```

  Compare your results for the relaxed H₂ molecule with data in the file `molecular.levels.h2_2.0.def-SV(P).dat` corresponding to the H-H distance of 2.0 a.u.

  **Question:** how did the energies of HOMO (highest occupied molecular level) and LUMO (lowest unoccupied molecular level) change? Why?

- Perform similar calculations with other basis sets (def-TZVP, def-QZVP). What are the equilibrium H-H bond lengths? Do results converge to the experimental value of 1.40 a.u.?
Further examples: try to do yourself!

- Following introduced strategy, compute potential energy profiles and equilibrium interatomic distances $d$ of diatomic molecules, $N_2$ and $O_2$:

  (i) modify script h2 accordingly, create new scripts, say n2 and o2, and compute energy profiles (choose $d$ in the range 1.75…6.0 a.u.)

  (ii) take energy minimum point, and invoke a script jobex to even better relax your molecule, compare your optimized interatomic distance with known experimental data (Google for it!)

- Remark: ground state of $N_2$ is closed shell (spin singlet, $S=0$), while the ground state of $O_2$ is a spin triplet ($S=1$, open shell)

Ask questions if you have problems, and enjoy!